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APPLICATION OF THE HERRING MODEL TO EXPLAIN THE IMPURITY CONTENT DEPENDENCE OF THE VISCOSITY OF QUARTZ GLASSES

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It is shown that the structural characteristics of quartz glasses make it possible to use the Herring model to describe their viscous flow, while the nonuniform distribution of impurities explains the known regularities in the dependence of the coefficient of viscosity on their content.

It is known that the mechanical properties of crystalline bodies are determined by dislocations and their mobility. All methods of hardening a crystalline material use a mechanism for stopping dislocation motion, specifically, by creating short-range order. In this case, C. Herring proposed a model for the mechanism of diffusion plasticity [1, 2] in which viscous flow is the result of plastic deformation of grains and depends on their size, i.e. on the scale of the structural nonuniformities. Under an anisotropic load, normal stresses which vary along the surface arise in each grain and result in a vacancy gradient. Vacancies diffuse, and in the process the shape of a grain changes. The self-consistent change in shape of grains results in a macroscopic change in the shape of the solid. A consequence of this flow mechanism is that the coefficient of viscosity depends on the grain size [1]:

$$\eta = kTd^2/(\theta D\Omega), \quad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, d is the grain size, $\theta = 0.1$ for relaxed tangential stresses at grain boundaries and $\theta = 4$ when relaxation is incomplete, D is the diffusion coefficient for vacancies, and Ω is the volume occupied by a single vacancy.

Optical and structural electron – microscopic studies have shown that all quartz glasses are structurally nonuniform irrespective of the technology used to produce them [3–7]. The authors of [6] attribute the discreteness to, for example, the possibility of the existence of chemical compounds of the type element – oxygen polyhedra in melt, where such compounds are formed “according to the princi-

ple of the construction of complex ions with the participation of oxygen, alkali or other sufficiently strongly basic oxides.”

In summary, the elements of nonuniformity already exist in the melt. As far as the buildup of volatile silicate compounds is concerned, silica particles which are formed in the burner flame grow even before interacting with the melt zone, and they undergo “definite transformations” in such an interaction [6]. As the melt temperature decreases, aggregation processes prevail and the “primary individuals” [6] possess a substantial surface energy, which limits the formation of secondary large particles.

Even if the impurity present in the initial material is distributed uniformly in it, the uniformity of its distribution is destroyed in the fused silica. Studying the stability of anionic complexes in silicon melt, the authors of [8] arrived at the conclusion that charged anionic complexes SiO_4^- arising in the presence of alkali oxide impurities should be present on the periphery of globular structures, consisting of highly polymerized tetrahedral $[\text{SiO}_4^0]$. This agrees with existing data on the nonuniform distribution of impurity in silica [4, 9]; in addition, the data of [9] can be regarded as direct proof of an enhanced impurity concentration in separate regions compared with the average concentration over the volume. Thus, the micro-nonuniformity of fused silica is manifested in a grainy structure, and in the case of impurity consisting of alkali-metal oxides the grains contain mainly “pure” silica and the impurity is concentrated on grain surfaces.

This suggests that C. Herring's flow mechanism proposed for materials with grainy structure is also applicable to quartz glasses, and the mobile elements making grain defor-

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mation possible are defects of the short-range order [10]. In pure silica, these are oxygen vacancies, and they are located inside the grain volume.

Other defects predominate at the periphery — nonbridging oxygen atoms, which comprise a grain boundary. These identical formations can capture and retain alkali-metal ions, so that there is a basis for supposing that the quantity of an impurity in the surface layer of a grain corresponds to its constant concentration. Then, each value of the volume-average impurity concentration in silica should correspond to a unique area of the total surface of the grains which is associated with their average size. This quantity depends not so much on the impurity content in the initial material as on the fusion technology.

The data of [11, 12] and other works where measurements of the impurity content in the batch and glass are presented can serve as examples. Even in glasses made from a batch with no added impurity, the impurity content differed by almost a factor of 3, and glasses in which the impurity concentration decreased by more than a factor of 2 and reached 0.1 of its concentration in the batch were obtained from a batch to which impurities were added. This can be explained by the fact that in the process of fusion in vacuum only the impurity which was secured by the previously mentioned anionic complexes located on grain boundaries remained in the glass. Since the surface area of the grains limits the amount of such complexes, the excess impurity evaporates.

When only alkali-metal oxides are present in glass, it is easy to establish a relation between the grain size and the volume-average impurity concentration by equating the impurity mass concentrated only in a surface layer to the amount of impurity that would uniformly fill the entire grain volume with average concentration c :

$$d = 6\delta c_0 / c, \quad (2)$$

where δ is the thickness of the surface layer and c_0 is the impurity concentration in the surface layer of a grain.

It is assumed that the thickness of the layer is independent of the diameter of a grain.

Substituting the expression (2) into Eq. (1) and taking

$$A = \frac{kT}{D\theta\Omega} (6\delta c_0)^2,$$

we obtain the dependence of the change in the coefficient of viscosity on the alkali oxide impurity content:

$$\eta = A/c^2. \quad (3)$$

The relation (3) agrees with the experimental dependence observed in [11], where the effect of various impurities on the viscosity of fused silica is studied. In this work it was also established that in quartz glasses containing only hydroxyl groups the dependence of the viscosity on the OH concentration is different:

$$\eta = B/c^{0.6}. \quad (4)$$

Adhering to C. Herring's model and assuming that there is a relation between grain size and impurity amount even in this case, one can talk about a different character of the impurity distribution in a grain: the impurity is concentrated at the center of the grain, occupying a region with radius δ which is independent of the grain size. Hence it follows that as the impurity content increases, the number of grains per unit volume increases, i.e., the grain size decreases. In this case the relation between the average impurity concentration in glass and the grain size is described by the expression

$$d = 2\delta(c_0/c)^{1/3}, \quad (5)$$

where c_0 is a constant impurity concentration at the center of a grain.

Using Eq. (5) and the expression (1) we obtain

$$\eta = B/c^{2/3}, \quad (6)$$

where $B = \frac{kT}{D\theta\Omega} (2\delta c_0)^{2/3}$.

Evidently, the exponents in the expressions (4) and (6) are close, and a more accurate approximation of the function $\eta(c)$ according to the data from [11] gives 0.65 for the exponent.

It is obvious that the impurities considered here not only "indicate" but also influence the grain size, settling on the surface or in the center of a grain. It is known that graininess is characteristic of pure silica: grains are formed even during fusion and continue to grow by coagulation. Consequently, a large variance of the viscosity is observed even in pure silica. Impurities R_2O create conditions that inhibit coagulation, because when they settle on the surface of grains they switch the free oxygen bonds to themselves. The hydroxyl components OH "displace" from the grain volume a certain fraction of oxygen vacancies onto the surface, likewise changing its coagulation properties.

In quartz glasses containing the impurities R_2O , OH, and Me_2O_3 (Me — Al, Ga) the character of the dependence is determined by the presence of R_2O [11]. The role of the remaining impurities reduces to changing the values of A and the activation energy. This shows that the grain size is determined primarily by impurities which are concentrated in the surface layer of grains, and if the impurity Me_2O_3 is present in this layer, then the R_2O concentration in the surface layer increases as result of the formation of the complexes $R^+[MO_{4/2}]^-$.

The results obtained in this work can serve as a basis for developing a method for analyzing the localization of impurities in glasses possessing a grainy structure.

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